ELEMENTARY RADIATION CHEMISTRY

BAEN-625 Advances in Food Engineering
The overall process of forming chemically stable products after the absorption and redistribution of the excess of energy of ionizing radiation.

The resulting compounds are radiolytic products.
STOCHASTIC NATURE OF ENERGY TRANSFER

- Mathematical formulations cannot describe the stochastic nature of electron track.
- The continuous slowing down approximation is inadequate to describe the events that lead to molecular alterations in the medium.
Energy transfer is generally the result of the deposition of energy in discrete events. These events are:
- Spur: from 6 to 100 eV
- Blob: from 100 to 500 eV
- Short track: from 500 to 5000 eV
Ionized, excited, or super excited are very unstable.

Electronic configurations are rearranged and interactions with other molecules occur.

The result of some of the secondary electrons scattering interactions, delta rays are also formed.
Electrons can interact with the secondary electrons creating a track of their own

- A 1MeV electron deposits
  - 65% of their energy in spurs
  - 15% in blobs
  - 20% in short tracks (scattered electrons with low KE)
SECONDARY ELECTRONS IN THE MEDIUM

- Deposit energy in randomly located, small interaction volumes
- One to a few reaction products are formed by the deposition of energy from the secondary electron
- Interaction may occur within small interaction volumes
- There are no interactions for reactions products between separate interaction sites (spurs, blobs, short tracks)
- The average spur is 1 nm in radius (in water it contains an average of six radical products)
Radiation Chemistry

- The direct effect of excitation and ionization of water by the secondary electron is the predominant reaction in biological systems for low LET radiation.

- The initial reactions occur on a time scale of $10^{-16}$ to $10^{-12}$ s.
PRIMARY PRODUCTS OF RADIOLYSIS

The ended result of this initial radiation chemistry of excitation and ionization in a water medium is:

\[ H_2O \rightarrow \cdot H_2O^+ + e_{aq}^- \quad \text{ionization} \]
\[ \rightarrow \cdot H + \cdot OH \quad \text{dissociation} \]
\[ \rightarrow H_2O^* \quad \text{excitation} \]
The immediate products of combination of the primary products with water molecules or hydrogen ions are as follows:

\[
\cdot H_2O^+ + e_{aq}^- \rightarrow \cdot H^+ + \cdot OH^- \\
H_2 + \cdot OH \rightarrow H_2O + \cdot H
\]
THE SOLVENT ELECTRON

- Or aqueous or hydrated electron, $e^{-}_{aq}$
- It is quite stable with respect to its reaction with water
- The reaction rate constant for reaction with water is about 200 mol s$^{-1}$
THE SOLVENT ELECTRON

- Electrons produced as the result of water ionization lose their kinetic energy by multiple interactions with their surrounding environment.
- After electrons are sufficiently slowed down, they attract the permanent dipole of several water molecules to form the hydrated electron.
- This new entity has a lifetime in neutral water of about $2 \times 10^{-4}$s.
- The hydrated electron is more stable than the free electron.
In the first ionization-excitation event of the fast electron, only two to five water molecules are ionized or excited.

These radicals or excited molecules are formed within a few nm of each other.

From $10^{-12}$ to $10^{-10}$ s the active species undergo the reactions given previously, lose their kinetic energy, and diffuse from their point of formation.
RECOMBINATION

- Immediate reaction that can occur while the reactive species are still very close to each other
- Conversion of their energy to thermal energy in the vicinity
- Radicals, as well as ion pairs, can recombine.
- With the passage of time, diffusion separates and effectively dilutes them in the water environment,
- Recombination is over in $10^{-11}$ s, after which diffusion controlled processes become important
After the thermalization of the various species formed in the early reactions, the third (or chemical) stage begins.

It lasts until all the chemical reactions have ended.

These reactions occur in the vicinity of the track and are nonhomogeneous; that is, the concentrations controlling the reaction rates are not uniform.

These reactions are enormously complex, and many of the reaction products are of little importance.
CHEMICAL STAGE

- For neutral water the list of products can be summarized in the following way (not balanced equations of course)

- $\text{H}_2\text{O}$ (irradiated)

\[
\Rightarrow H, e_{aq}^-, OH, H_3O^+, H_2, OH^-
\]

\[
H_2O_2, O_2, O_2, HO_2^-, H_2O_2, O_2^-
\]
CHEMICAL STAGE

- At $10^{-12}$ s the four chemically active species ($\text{H}_2\text{O}^+$, OH, $\text{e}_{\text{aq}}$, H) are located near the positions of the original $\text{H}_2\text{O}^+$, $\text{H}_2\text{O}^*$, and $\text{e}^-$.
- Three of the new reactants (OH, $\text{e}_{\text{aq}}$, H) are free radicals.
- The reactants begin to migrate randomly.
(1) OH + OH $\Rightarrow$ H$_2$O$_2$
(2) OH + $e^-_{aq}$ $\Rightarrow$ OH$^-$
(3) OH + H $\Rightarrow$ H$_2$O
(4) H$_3$O$^+$ + $e^-_{aq}$ $\Rightarrow$ H + H$_2$O
(5) $e^-_{aq}$ + $e^-_{aq}$ + 2H$_2$O $\Rightarrow$ H$_2$ + 2OH$^-$
(6) $e^-_{aq}$ + H + H$_2$O $\Rightarrow$ OH$^-$ + H$_2$
(7) H + H $\Rightarrow$ H$_2$
CHEMICAL STAGE

- By $10^{-6}$ s the reactants diffuse so far away from another so the probability of additional reactions is small.
- The chemical development of the track in pure water then is over.
The motion of the reactants can be viewed as a random walk.

If $D_o$ is the measured diffusion constant for a species, then, on the average it will move a small distance $\lambda$ in time $\tau$:

$$\frac{\lambda^2}{6\tau} = D_o$$
Each type of reactive species can be regarded as having a reaction radius

Two species that approach each other closer than the sum of their reactive radii have a change to interact according to previous reaction equations

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0 \times 10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>$R[A]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>2</td>
<td>2.4</td>
</tr>
<tr>
<td>$e_{aq}$</td>
<td>5</td>
<td>2.1</td>
</tr>
<tr>
<td>$H_3O^+$</td>
<td>8</td>
<td>0.30</td>
</tr>
<tr>
<td>H</td>
<td>8</td>
<td>0.42</td>
</tr>
</tbody>
</table>
It is a convenient means to compare relative yields of various chemical species as the result of deposition of energy from ionizing particles.

It is defined as the number of molecules formed (or destroyed) per 100 eV of energy absorbed.
<table>
<thead>
<tr>
<th>Products</th>
<th>G-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>e(_{aq})</td>
<td>2.6</td>
</tr>
<tr>
<td>H</td>
<td>0.6</td>
</tr>
<tr>
<td>OH</td>
<td>2.6</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.45</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>0.75</td>
</tr>
</tbody>
</table>
$N_m = 10^{-7} GM_w D$

$N_m$ = species/molecule  
$G$ = G-value  
$M_w$ = molecular weight  
$D$ = dose [kGy]
For water, with dose of 1 kGy, the probability of creating OH radical from a single water molecule is

\[ N_m = 10^{-7} (2.7)(18)(1) \]

\[ = 5 \times 10^{-6} \]

Quite small
The scavenger, which can be any molecular species capable of interaction, reacts with the radicals to bring the water chemistry to an end.

For low concentrations of any scavenger molecule, the fraction of the radicals that interacts with the scavenger is nearly constant over a wide range of scavenger concentration.
FOOD IRRADIATION

- Water is a large component of most foods
- \( e^-, 'H, 'OH \) are very reactive species
- The only stable end products are
  - \( \text{H and } H_2O_2 \)
- However these are largely consumed through reactions

\[
H_2O_2 + e^- \rightarrow \cdot OH + OH^- \\
H_2 + \cdot OH \rightarrow H_2O + \cdot O
\]
Water radiolysis can be expected to cause oxidation and reducing reactions

- Hydroxyl radical is a powerful oxidizing agent
- Hydrated electron is a strong reducing agent
\[ H_2O \rightarrow \cdot OH(2.6) + e^-_{aq}(2.6) + \cdot H(0.6) + H_2(0.45) + H_2O_2(0.75) \]